to indicate the absence of a complex acid, for Hildebrand and Bowers[1] were able to show the existence of halogen acids of zinc, of the type $HZnCl_3$, by this method, which they devised.

(3) The action of hydrogen sulfide on solutions of stannic tin containing large quantities of alkali fluorides seems to indicate that in this case, where we have ideal conditions for the formation of a complex, we are able to precipitate the tin practically completely, although slowly.

Summary.

Stannic fluoride has been prepared with a minimum use of platinum ware. Experiments have established the facts that this compound has a slight initial dissociation, as indicated by conductivity measurements, and that the compound hydrolyzes much less rapidly than does stannic chloride in solutions of the same normality.

Reasoning from the results of the experiments on the hydrolysis of stannic fluoride, and from facts encountered in other experiments with solutions of stannic fluoride containing alkali fluorides, or free hydrofluoric acid, there has been advanced a possible explanation of the mechanism whereby tin, and a number of elements which act in similar manner, in hydrofluoric acid solution, are prevented from being precipitated by various reagents.

The writer wishes to thank Dr. L. W. McCay for interest and guidance and to thank other members of the Chemical Department of Princeton University for valuable advice, during the progress of this work.

PRINCETON, N. J.

[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK.]

THE DETECTION OF IODIDES IN THE PRESENCE OF CYANIDES.

BY L. J. CURTMAN AND C. KAUFMAN.

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The object of this investigation was twofold: first, to determine the extent of the interfering influence of cyanides in the test for iodides by the use of oxidizing agents; second, to provide a rapid and reliable method whereby one mg. of iodide could be detected in the presence of 500 mg. of cyanide.

Determination of the Amount of Interference.—In the presence of limited amounts of cyanide, iodine is visibly liberated by potassium nitrite as well as by other oxidizing agents. The reddish brown coloration which the liberated iodine imparts to the solution disappears, how-

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[1] "A Study of the Action of Alkali on Certain Zinc Salts by Means of the Hydrogen Electrode," THIS JOURNAL, 38, 785 (1916).

ever, after some time, the speed of disappearance varying with the amount of cyanide present. In connection with this observation, the following experiment is of interest: To a test tube were added successively one mg. iodine as potassium iodide, 0.4 mg. cyanide as potassium cyanide, 6 drops of 10% potassium nitrite, one cc. of starch solution and sufficient water to bring the volume up to 5 cc.; 4 drops of 10% hydrochloric acid were then added. At the same time 2 controls were run, one containing no cyanide and the other no iodide. In the tube containing both iodide and cyanide, a deep blue precipitate formed immediately on the addition of the acid. After some time, the blue color disappeared from all but a small portion that had settled to the bottom. On shaking slightly, however, the color entirely disappeared. The first control gave a deep blue permanent precipitate. The second remained colorless. It appears from these experiments, that although iodine may be visibly liberated in the presence of cyanide, it enters into combination again. In this connection it is of interest to note that the further addition of the oxidizing agent failed to liberate any iodine from the reaction mixture. A similar observation was made in attempts to liberate bromine by chlorine water in the presence of thiocyanate.[1]

Preliminary experiments to determine the amount of interference gave results which varied with the time which elapsed between the addition of the reagent liberating iodine and the shaking of the solution. The greater this interval, the smaller was the quantity of cyanide which prevented the detection of 1 mg. iodine. On the other hand, when the mixtures were shaken immediately after the addition of the oxidizing agent, closely concordant results could not be obtained; for these reasons a 5-minute interval was adopted.

A successful determination of the amount of interference was secured by the following procedure: From a graduated pipet, one cc. of standard potassium iodide solution (1 cc. = 1 mg. I) was introduced into a test tube. To this were added successively a definite volume of a standard potassium cyanide solution, one cc. of chloroform, 5 drops of 10% potassium nitrite, sufficient water to bring the volume to 5 cc. and 3 drops of 10% hydrochloric acid. The tubes were allowed to stand for 5 minutes and then shaken. The same procedure was followed to determine the interference of cyanides when hydrogen peroxide, potassium permanganate and chlorine water were, respectively, employed as iodine liberators. The results obtained are given in Table I.

The results of Table I clearly show that there is interference with each of the oxidizing agents tried and of these the interference is least with potassium permanganate.

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[1] Curtman and Wikoff, THIS JOURNAL, 37, 299 (1915).

Table I.—Interference of Cyanides.

1 mg. I as KI; 1 cc. $CHCl_3$; 3 drops 10% HCl; Vol. 5 cc.

10% KNO_2,[1] 5 drops.		0.5% $KMnO_4$,[2] 2 drops.		Sat. Cl water, 2 drops.		2% H_2O_2, 5 drops.	
Mg. CN.	Test.	Mg. CN.	Test.	Mg. CN.	Test.	Mg. CN.	Test.
0.4	Neg.	30	Doubtful	20	Neg.	8	Neg.
0.3	Very faint	25	Very faint	10	Doubtful	7	Neg.
0.2	Fair	15	Faint	7	Faint	6	Faint
0.1	Good	10	Fair			4	Fair
		5	Good			1	Fair

Since in actual practice the reaction mixture is shaken immediately after the addition of the last reagent, the interference will not be as great as the above figures indicate. To form an idea of the interference in routine work, another set of experiments was run in which the solutions were shaken immediately after the addition of the potassium permanganate. Under these conditions, about twice as much cyanide is permissible.

Method for the Detection of Iodides in the Presence of Cyanides.—In a previous communication[3] from this laboratory, cobalt nitrate was successfully used to precipitate cyanides, ferrocyanides and ferricyanides, the well-known difficulties of filtration being surmounted by the addition of asbestos fiber. These features were embodied in the present method. The solution, the volume of which should be about 25 cc., is treated with an excess of cobalt nitrate solution.[4] After adding 3 g. of washed asbestos fiber, the mixture is boiled for one-half minute with stirring, and filtered. The precipitate is washed twice with small amounts of water; the filtrate and washings, after concentration by evaporation, to about 4 cc., are transferred to a test tube. The dish is rinsed with 2 cc. of water and the rinsings united with the solution in the test tube. The test for iodides is then made by adding 1 cc. of chloroform, 2 cc. 3 *N* sulfuric acid and 2 drops of 0.5% potassium permanganate. A violet color in the chloroform layer, after shaking, proves the presence of iodide. The following test analyses show the method to be reliable:

Test Analyses.

Anal. No.	Mg. CN.	Mg. I.	Result.
1– 5	500	0.0	Negative
6–10	500	1.0	Positive

Summary.

1. A study has been made of the interference of cyanides in the test for iodides.

2. Data are supplied showing the extent of the interference when ni-

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[1] In these experiments the HCl was always added last.

[2] 2 cc. 3 *N* H_2SO_4 were used in place of 3 drops of dil. HCl.

[3] Curtman and Harris, This Journal, 38, 2625 (1916).

[4] This solution contained 25 g. $Co(NO_3)_2.6H_2O$ in 100 cc.

trite, hydrogen peroxide, saturated chlorine water and potassium permanganate are, respectively, used to liberate the iodine.

3. A rapid and reliable method is proposed which is capable of detecting one mg. iodine as iodide in the presence of 500 mg. of cyanide.

[Contribution from the Chemical Laboratory of the University of Wisconsin.]

A STUDY OF THE CHEMISTRY OF GOLD AT HIGH TEMPERATURES AND PRESSURES.[1]

By Harold H. Morris.

Received April 2, 1918.

This contribution to the chemistry of gold is the result of one of a series of investigations undertaken in the chemical laboratory of the University of Wisconsin on the deposition and alteration of various minerals due to the effects of heat and of aqueous vapor pressure. A particular study was made of the compounds of gold because of the relation of such a study to the theories concerning the deposition of gold in nature.[2]

The apparatus used here is described in detail, since it is expected that only slight modifications will be necessary in carrying on further work in this field. It consisted of an electrically heated steel bomb, and a platinum platinum-rhodium thermocouple used in connection with a potentiometer for temperature measurements.

The steel bomb was of the general type of the Morey bomb,[3] the several parts of which are shown in cross section in Fig. 1, which is drawn to scale. The material used in the construction was electric chrome-vanadium steel. The three principal parts of the bomb are A, B and E. The body

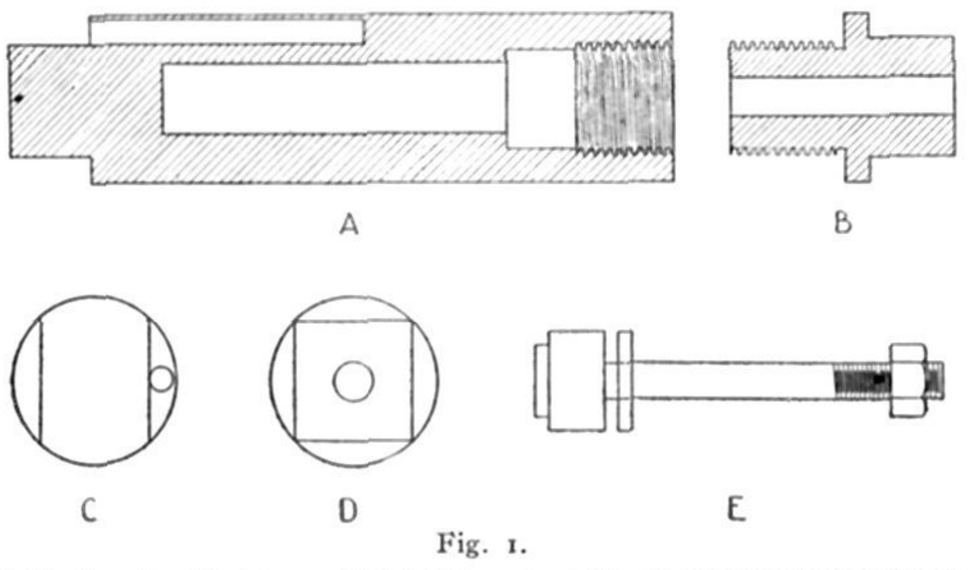

Fig. 1.

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[1] A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Lenher and Morris, *Econ. Geol.*, [3] 13, 161.

[3] Morey, This Journal, 26, 215 (1914).